

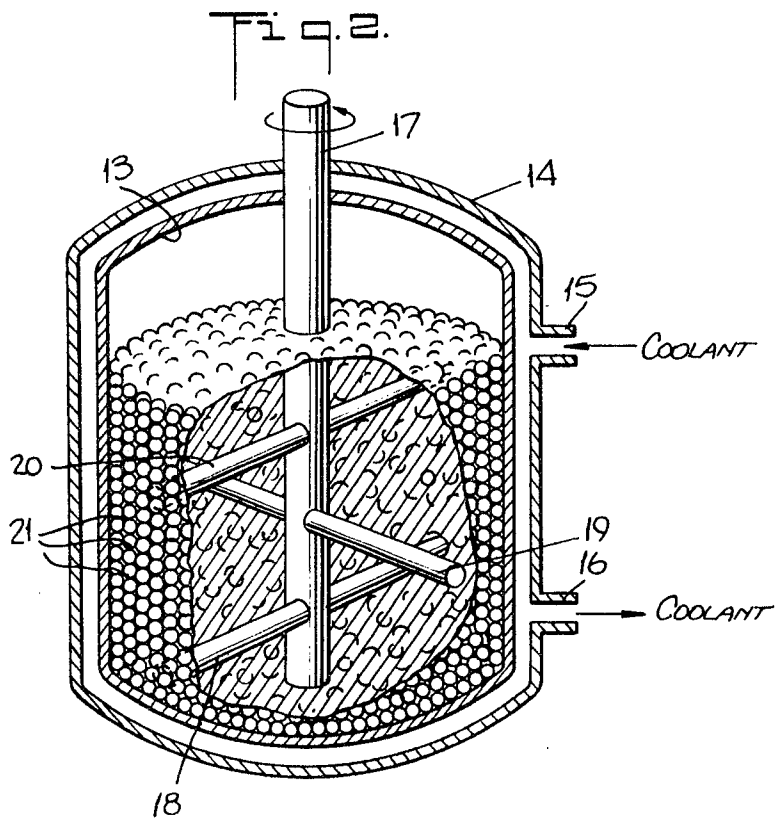
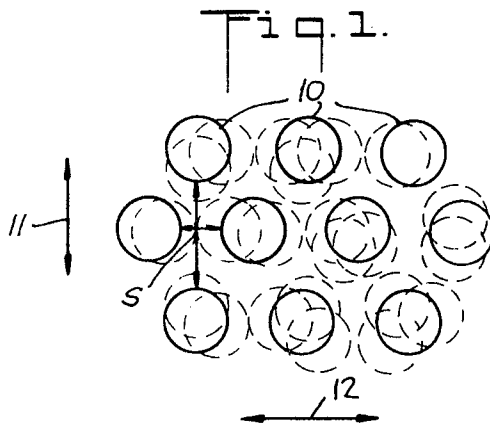
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HIGH CARBON TOOL STEELS BY POWDER METALLURGY

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HIGH CARBON TOOL STEELS BY POWDER METALLURGY

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7 Claims

ABSTRACT OF THE DISCLOSURE

This application relates to the powder metallurgy of wrought, high carbon tool steels and also to a powder metallurgy method for producing said steels characterized metallographically by a uniform distribution of finely divided carbides in both the longitudinal and transverse directions.

This application is a continuation-in-part of U.S. application Ser. No. 709,700, filed Mar. 1, 1968.

THE RELATED APPLICATION

In the aforementioned related application, Ser. No. 709,700, which is incorporated herein by reference, a method is disclosed for producing a wrought composite metal powder comprised of a plurality of constituents mechanically alloyed together, at least one of which is a metal capable of being compressively deformed such that substantially each of the particles is characterized metallographically by an internal structure comprised of the starting constituents intimately united together and identifiably mutually interdispersed. One embodiment of a method for producing the composite powder resides in providing a dry charge of attritive elements and a powder mass comprising a plurality of constituents, at least one of which is a metal which is capable of being compressively deformed. The charge is subjected to agitation milling under high energy conditions in which a substantial portion or cross section of the charge is maintained kinetically in a highly activated state of relative motion and the milling continued to produce wrought composite metal powder particles of substantially the same composition as the starting mixture characterized metallographically by an internal structure in which the constituents are identifiable and substantially mutually interdispersed within substantially each of the particles. The internal uniformity of the particles is dependent on the milling time employed. By using suitable milling times, the interparticle spacing of the constituents within the particles can be made very small so that when the particles are heated to an elevated diffusion temperature, interdiffusion of diffusible constituents making up the matrix of the particle is effected quite rapidly.

Tests have indicated that the foregoing method enables the production of metal systems in which insoluble non-metallics such as refractory oxides, carbides, nitrides, silicides, and the like, can be uniformly dispersed throughout the metal particle. In addition, it is possible to interdisperse alloying ingredients within the particles, particularly large amounts of alloying ingredients, e.g., such as chromium, which have a propensity to oxidize easily due to their rather high free energy of formation of the metal oxide. In this connection, mechanically alloyed powder particles can be produced by the foregoing method containing any of the metals normally difficult to alloy with another metal.

THE PRIOR ART

High carbon tool steels are produced conventionally by melting, casting of the molten metal into an ingot, and

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then, after subjecting the ingot to the usual soaking treatment at an elevated temperature followed by surface cleaning, hot working the ingot by stages to the desired shape. Freezing of an ingot plays an important part in the quality of the final product, namely, segregation. Complex alloys, particularly high carbon, high alloy tool steels may suffer from several kinds of segregation which can have an adverse effect on the forgeability of the ingot and on its metallographic structure. In the molten condition, high carbon alloy steels are partially uniform throughout, the various elements present, such as carbon, silicon, manganese, chromium, vanadium, tungsten, molybdenum, and the like, being essentially dissolved. Since ingots produced in practice are generally large, selective solidification takes place during freezing, leading to composition segregation along the length and the width of the ingot. Unless this is removed by subsequent treatment, the alloy may exhibit non-uniform response to heat treatment.

Moreover, during freezing, large dendrites and carbide segregates and/or aggregates may form in the ingot. After solidification of the ingot, such segregates and/or aggregates may be broken up with difficulty by mechanical work. However, such carbides are generally brittle and adversely affect the ductility of the ingot. Where the formation of carbide segregates and aggregates is rather marked in the ingot, the carbide distribution appears as elongated structures in the forged or hot worked product in the longitudinal direction with areas therebetween impoverished in carbides. Such metallurgical structures are not desirable and can have an adverse effect on the physical properties.

Attempts have been made to utilize powder metallurgy techniques as an alternative method for producing high carbon tool steels free from coarse dendrites and segregates characteristic of the conventional melting and casting practice. However, it has been difficult to obtain good composition homogeneity by solid state diffusion at elevated temperatures due to diffusion sluggishness of such alloying ingredients as chromium, tungsten, molybdenum, etc., in the powder condition. While the diffusion path of the elements can be decreased by using very small particle sizes, for example 2 or 1 micron powder, such sizes tend to be pyrophoric and hence easily subject to contamination by reaction with the environment, e.g., air.

While many attempts have been made to produce high carbon high alloy tool steel having optimum composition uniformity, having good response to heat treatment, and having a uniform dispersion of finely divided carbide throughout the steel, none, as far as I am aware, has been wholly successful prior to the present invention.

It is thus an object of this invention to provide a powder metallurgy method for producing a wrought, high carbon tool steel characterized by a high degree of composition uniformity and by optimum response to heat treatment.

Another object is to provide a powder metallurgy method for producing a wrought, high carbon high alloy tool steel product in which contamination during the early stages of manufacture is not a problem.

A further object is to provide a powder metallurgy method for producing a high carbon, high alloy tool steel characterized metallographically by a uniform dispersion of finely divided carbide and being free of carbide segregates and/or aggregates.

This invention also provides as an object a powder metallurgy produced wrought high carbon tool steel characterized by a high degree of composition uniformity, by optimum response to heat treatment, by a uniform dispersion of finely divided carbide and further character-

ized in being substantially free from carbide segregates and/or aggregates.

These and other objects will more clearly appear when taken in conjunction with the following description and the accompanying drawing, wherein:

FIG. 1 depicts schematically a portion of a ball charge in a kinetic state of random collision; and

FIG. 2 is a schematic representation of an attritor of the stirred ball mill type capable of providing agitation milling to produce composite metal particles employed in carrying out the invention.

STATEMENT OF THE INVENTION

In its broad aspects, the present invention is directed to the powder metallurgy production of a wrought high carbon tool steel product characterized substantially by uniform composition throughout, by a uniform dispersion of finely divided carbide, and further characterized in being substantially free from carbide segregates and/or aggregates. In its more preferred aspects, the invention provides a high carbon tool steel product characterized by a high degree of carbide dispersion substantially free from carbide segregates and/or aggregates in both the longitudinal and transverse cross sections and, particularly, in any selected area when viewed in magnification of up to 10,000 times or more. Such uniformity results from the use of a dense, wrought, metal composite particle having a highly uniform internal structure. In other words, by starting with the foregoing composite particles as the building blocks in producing the wrought metal shape, the high degree of uniformity of each of the composite particles is carried forward and maintained in the final wrought product with substantially no carbide segregates and/or aggregates in the internal structure.

For the purposes of this invention, it is advantageous that the product contains less than 10 volume percent of segregated regions exceeding 25 microns in minimum dimension. A segregated region is one in which there is a significant composition fluctuation exceeding 25 microns or even 10 microns, in size. A significant composition fluctuation is defined as a deviation exceeding 10% of the mean content of the alloying element present. The size of the segregated regions is measured as the minimum distance through the segregated region between adjacent positions bounding the segregated region at a composition deviation one-half of the maximum fluctuation of the amount present.

The wrought composite metal particles which are employed in the starting material are defined in copending application Ser. No. 709,700 as being made by integrating together into dense particles a plurality of constituents in the form of powders, at least one of which is a compressively deformable metal. The requirement of deformable metal is fulfilled by iron since it constitutes essentially the balance of the steel composition. In one method, the constituents are intimately united together to form a mechanical alloy within individual particles without melting any one or more of the constituents. Thus, the formation of carbide segregates, dendrites and/or aggregates is substantially avoided. By the term "mechanical alloy" is meant that state which prevails in a composite metal particle wherein a plurality of constituents in the form of powders, at least one of which is a compressively deformable metal, are caused to be bonded or united together, according to one method, by the application of mechanical energy in the form of a plurality of repeatedly applied compressive forces sufficient to vigorously work and deform at least one deformable metal and cause it to bond or weld to itself and/or to the remaining constituents, be they metals and/or non-metals, whereby the constituents are intimately united together. By repeated fracture and rewelding together of the composite particles thus formed a fine codissemination of the fragments of the various con-

stituents throughout the internal structure of each particle is achieved. Concurrently, the overall particle size distribution of the composite particles remains substantially constant throughout the processing. By observation of the grinding media, e.g., balls, during processing, it appears that the major site at which welding and structural refinement of the product powder takes place is upon the surfaces of the balls.

The process employed for producing mechanically alloyed particles comprises providing a mixture of a plurality of powdered constituents, at least one of which is a compressively deformable metal, and at least one other constituent is selected from the group consisting of a non-metal and another chemically distinct metal, and subjecting the mixture to the repeated application of compressive forces, for example, by agitation milling as one method under dry conditions in the presence of attritive elements maintained kinetically in a highly activated state of relative motion, and continuing the dry milling for a time sufficient to cause the constituents to comminute and bond or weld together and codisseminate throughout the resulting metal matrix of the product powder. The mechanical alloy produced in this manner is characterized metallographically by a cohesive internal structure in which the constituents are intimately united to provide an interdispersion of comminuted fragments of the starting constituents. Generally, the particles are produced in a heavily cold worked condition and exhibit a microstructure characterized by closely spaced striations.

It has been found particularly advantageous in obtaining optimum results to employ agitation milling under high energy conditions in which a substantial portion of the mass of the attritive elements is maintained kinetically in a highly activated state of relative motion. However, the milling need not be limited to such conditions so long as the milling is sufficiently energetic to reduce the thickness of the initial metal constituents to less than one-half of the original thickness and, more advantageously, to less than 25% of the average initial particle diameter thereof by impact compression resulting from collisions with the milling medium, e.g., grinding balls.

As will be appreciated, in processing powder in accordance with the invention, countless numbers of individual particles are involved. Similarly, usual practice requires a bed of grinding media containing a large number of individual grinding members, e.g., balls. Since the particles to be contacted must be available at the collision site between grinding balls or between grinding balls and the wall of the mill or container, the process is statistical and time dependent.

By the term "agitation milling," or "high energy milling" is meant that condition which is developed in the mill when sufficient mechanical energy is applied to the total charge such that a substantial portion of the attritive elements, e.g., ball elements, are continuously and kinetically maintained in a state of relative motion with each other; that is to say, maintained kinetically activated in random motion so that a substantial number of elements repeatedly collide with one another. It has been found advantageous that at least about 40%, e.g., 50% or 70% or even 90% or more, of the attritive elements should be maintained in a highly activated state.

Since generally the composite metal particles produced in accordance with the invention exhibit an increase in hardness with milling time, it has been found that, for purposes of this invention, the requirements of high energy milling are met when a powder system of carbonyl nickel powder mixed with 2.5 volume percent of thoria is milled to provide within 100 hours of milling and, more advantageously, within 24 hours, a composite metal powder whose hardness increase with time is at least about 50% of substantially the maximum hardness increase capable of being achieved by the milling. Putting it another way, high energy milling is that condition which will achieve in the foregoing powder system an

increase in hardness of at least about $\frac{1}{2}$ of the difference between the ultimate saturated hardness of the composite metal particle and its base hardness, the base hardness being that hardness determined by extrapolating to zero milling time a plot of hardness data obtained as a function of time up to the time necessary to achieve substantially maximum or saturation hardness. The resulting composite metal particles should have an average particle size greater than 3 microns and, more advantageously, greater than 10 microns, with preferably no more than 10% by weight of the product powder less than one micron.

By maintaining the attritive elements in a highly activated state of mutual collision in a substantially dry environment and throughout substantially the whole mass, optimum conditions are provided for comminuting and cold welding the constituents accompanied by particle growth, particularly with reference to the finer particles in the mix, to produce a mechanically alloyed structure of the constituents within substantially each particle. Where at least one of the compressively deformable metallic constituents has an absolute melting point substantially above about 1000°K ., the resulting composite metal powder will be heavily cold worked due to impact compression of the particles arising from the repeated collision of elements upon the metal particles. For optimum results, an amount of cold work found particularly useful is that beyond which further milling does not further increase the hardness, this hardness level having been referred to hereinbefore as "saturation hardness." This saturation hardness is typically far in excess of that hardness obtainable in bulk metals of the same composition by such conventional working techniques as cold forging, cold rolling, etc. The saturation hardness achieved in pure nickel processed in accordance with this invention is about 477 kg./mm.^2 as measured by a Vickers' microhardness tester, while the maximum hardness obtained by conventional cold working of bulk nickel is about 250 kg./mm.^2 . The values of saturation hardness obtained in processing alloy powders in accordance with this invention frequently reach values between 750 and 850 kg./mm.^2 as measured by Vickers' microhardness techniques. Those skilled in the art will recognize the amazing magnitude of these figures. The saturation hardness obtained in powders processed in accordance with this invention is also far in excess of the hardnesses obtained in any other process for mixing metal powders.

As illustrative of one type of attritive condition, reference is made to FIG. 1 which shows a batch of ball elements **10** in a highly activated state of random momentum by virtue of mechanical energy applied multidirectionally as shown by arrows **11** and **12**, the transitory state of the balls being shown in dotted circles. Such a condition can be simulated in a vibratory mill. Another mill is a high-speed shaker mill oscillated at rates of up to 1200 cycles or more per minute wherein attritive elements are accelerated to velocities of up to about 300 centimeters per second (cm./sec.).

A mill found particularly advantageous for carrying out the invention is a stirred ball mill attritor comprising an axially vertical stationary cylinder having a rotatable agitator shaft located coaxially of the mill with spaced agitator arms extending substantially horizontally from the shaft. A mill of this type is described in the Szegvari U.S. Pat. No. 2,764,359 and in Perry's Chemical Engineer's Handbook, fourth edition, 1963, at pages 8-26. A schematic representation of this mill is illustrated in FIG. 2 of the drawing which shows in partial section an upstanding cylinder **13** surrounded by a cooling jacket **14** having inlet and outlet ports **15** and **16**, respectively, for circulating a coolant, such as water. A shaft **17** is coaxially supported within the cylinder by means not shown and has horizontal extending arms **18**, **19** and **20** integral therewith. The mill is filled with attritive elements, e.g., balls

21, sufficient to bury at least some of the arms so that, when the shaft is rotated, the ball charge, by virtue of the agitating arms passing through it, is maintained in a continual state of unrest or relative motion throughout the bulk thereof.

The dry milling process of the invention is statistical and time dependent as well as energy input dependent, and milling is advantageously conducted for a time sufficient to secure a substantially steady state between the particle growth and particle comminution factors. If the specific energy input rate in the milling device is not sufficient, such as prevails in conventional ball milling practice for periods up to 24 or 36 hours, a compressively deformable powder will generally not change in apparent particle size. It is accordingly to be appreciated that the energy input level should advantageously exceed that required to achieve particle growth, for example, by a factor of 5, 10, or 25, such as described for the attritor mill hereinbefore. In such circumstances, the ratio of the grinding medium diameter to the average particle diameter is large, e.g., at least 20 times or more. Thus, using as a reference a mixture of carbonyl nickel powder having a Fisher subsieve size of about 2 to 7 microns mixed with about 2.5% by volume of less than 0.1 micron thoria powder, the energy level in dry milling in the attritor mill, e.g., in air, should be sufficient to provide a maximum particle size in less than 24 hours. A mill of the attritor type with rotating agitator arms and having a capacity of holding one gallon volume of carbonyl nickel balls of plus $\frac{1}{4}$ inch and minus $\frac{1}{2}$ inch diameter with a ball-to-powder volume ratio of about 20 to 1, and with the impeller driven at a speed of about 180 revolutions per minute (r.p.m.) in air, will provide the required energy level.

The milling time t required to produce a satisfactory dispersion; the agitator speed W (in r.p.m.); the radius, r , of the cylinder (in cm.) and the volume ratio R of balls to powder are related by the expression:

$$1/t = KW^3r^2R$$

where K is a constant depending upon the system involved. Thus, once a set of satisfactory conditions has been established in one mill of this type, other sets of satisfactory conditions for this and other similar mills may be predicted by use of the foregoing expression. When dry milled under these energy conditions without replacement of the air atmosphere, the average particle size of the reference powder mixture will increase to an average particle size of between about 100 to 125 microns in about 24 hours. A conventional ball mill generally accomplishes a mixing of the powders with some incidental flattening of the nickel powders and negligible change in product particle size after up to 24 or 36 hours grinding in air.

Attritor mills, vibratory ball mills, planetary ball mills, and some ball mills depending upon the ball-to-powder ratio and mill size, are capable of providing energy input within a time period and at a level required in accordance with the invention. In mills containing grinding media, it is preferred to employ metal or cermet elements or balls, e.g., steel, stainless steel, nickel, tungsten carbide, etc., of relatively small diameter and of essentially the same size. The volume of the powders being milled should be substantially less than the dynamic interstitial volume between the attritive elements, e.g., the balls, when the attritive elements are in an activated state of relative motion. Thus, referring to FIG. 1, the dynamic interstitial volume is defined as the sum of the average volumetric spaces S between the balls while they are in motion, the space between the attritive elements or balls being sufficient to allow the attritive elements to reach sufficient momentum before colliding. In carrying out the invention, the volume ratio of attritive elements to the powder should advantageously be over about 4 to 1, and, more advantageously, at least about 10 to 1, so long as the volume of powder does not exceed about one-quarter of the dynamic inter-

stitial volume between the attritive elements. It is preferred in practice to employ a volume ratio of about 12 to 1 to 50 to 1.

be produced by the invention, Tables I and II are given. Iron is not listed in the tables, it being essentially the balance of each of the compositions listed.

TABLE I

Type steel	Nominal composition, percent by weight								
	C	Mn	Si	Cr	Ni	V	W	Mo	Co
Chromium.....	.85-1.0	0.6-0.8	0.1-0.4	0.15-0.3					
Chromium-molybdenum.....	0.9-1.25	0.3-0.7	0.1-0.4	1.1-1.5				0.3-0.5	
Chromium-Nickel.....	0.9-1.1	0.3-0.5	0.1-0.4	0.5-0.8	1.2-1.6				
Tungsten-finishing steel.....	1.25-1.40	0.1-0.4	0.1-0.5	0.2-0.4			3.25-4.0	0.2-0.4	
Semihigh speed steels.....	1.15-1.25	0.1-0.4	0.1-0.4	3.75-4.25			3-3.3	4.0-4.5	
	1.35-1.45						3.0-4.4	4.0-4.5	
	1.05-1.15						3.75-4.25	2.3-2.7	2.4-2.8
Air-hardening die steels.....	0.9-1.05	0.4-0.85	0.1-0.4	4.75-5.25		0.15-0.5		0.9-1.15	
High carbon, high chromium die steels.....	1.4-1.6	0.2-0.4	0.1-0.4	11-5.12.5		0.2-1.0		0.7-0.9	
	2.1-2.3								
	2.0-2.2								
Wear resistant die steels.....	2.15-2.5	0.3-0.8	0.3-0.8	5-5.5		3.75-5.0	0.6-0.9	0.8-1.3	
	2.1-2.3	0.3-0.5	0.1-0.4	3.75-4.25					
Special wear resistant die steel.....	3.25	0.3	0.3	1.0		12.0		1.0	

TABLE II

Type steel	Nominal composition, percent by weight								
	C	Mn	Si	Cr	Ni	V	W	Mo	Co
Tungsten types.....	0.8-0.85	0.1-0.4	0.1-0.4	4-4.25		2-2.15	18-18.5	0.5-0.75	
	0.95-0.98			4-4.25		2-2.15	18-18.5	0.5-0.75	
	0.97-1.03			3.75-4.25		2.8-3.2	13.5-14.5	0.65-0.85	
Tungsten-cobalt types.....	0.7-0.75	0.1-0.4	0.1-0.4	4-4.5		1.0-1.25	18-19	0.6-0.8	4.75-5.25
	1.5-1.6			4.5-4.75		4.75-5.0	12.5-13.5	0.4-0.6	4.75-5.25
	0.75-0.85			4.0-4.5		1.6-2.0	18.75-20.5	0.6-0.8	11-12.25
Molybdenum types.....	0.75-0.85	0.1-0.4	0.1-0.4	3.75-4.0		1-1.25	1.5-1.65	8-9	
	0.97-1.03			3.75-4.0		1.9-2.1	1.5-1.75	8.5-8.75	
	0.8-0.85			3.75-4.25		1.1-1.4	1.5-1.8	8.25-8.5	4.75-5.25
Molybdenum-cobalt types.....	0.87-0.93	0.1-0.4	0.1-0.4	3.5-4.0		1.85-2.25	1.3-1.6	8.45-8.95	8-8.5
	1.05-1.1			4-4.25		2.4-2.55	6-6.25	5.7-6.25	
	1.25-1.3			4.25-4.5		3.75-4.25	5.5-6.0	4.5-4.75	
Tungsten-molybdenum types.....									
Tungsten-molybdenum-cobalt types.....	1.5-1.6	0.1-0.4	0.1-0.4	4.0-4.75		4.75-5.25	6.25-6.75	3.0-5.0	4.75-5.25
Self-hardening type.....	2.25	1.5	0.25	2.0			11.0		

The deformable metals in the mixture are thus subjected to a continual kneading action by virtue of impact compression imparted by the grinding elements, during which individual metal components making up the starting powder mixture become comminuted and fragments thereof are intimately united together and become mutually interdispersed to form composite metal particles having substantially the average composition of the starting mixture.

The product powders produced in accordance with the invention have the advantage of being non-pyrophoric, i.e., of not being subject to spontaneous combustion when exposed to air. Indeed, the product powders are sufficiently large to resist substantial surface contamination when exposed to air.

The product particles may have a size of up to about 500 microns with a particle size range of about 3 to about 200 microns being more common when the initial mixture contains a major proportion of an easily deformable metal, such as iron. The relatively large particle size and low surface area which characterize the composite particles is an outstanding advantage in powder metallurgy processes requiring vacuum degassing for removing adsorbed or absorbed gases. The significance of this advantage becomes particularly marked when it is considered that certain fine metal particles absorb as much as 10 times the volume of gas present in the interstitial spaces between the powder particles.

DETAIL ASPECTS OF THE INVENTION

The foregoing procedure is particularly applicable to the production of high carbon alloy tool steels and, in particular, high carbon, high alloy tool steels.

As stated hereinbefore, the powder mixture may comprise a plurality of constituents so long as at least one is compressively deformable. In order to produce the desired composite particles, the ductible metal should comprise at least about 15%, or 25% or 50% or more by volume of the total composition. Where two or more compressively deformable metals are present, it is to be understood that these metals together should comprise at least about 15% by volume of the total composition.

As examples of wrought high carbon tool steels that can

Broadly stated, the compositions covered by this invention range by weight from about 0.7% to 4% carbon, at least about 0.1% of at least one alloying element from the group consisting of chromium, vanadium, tungsten and molybdenum and the balance essentially iron, for example, about 40%, 45% or 50% or more iron.

A composition range to which the invention is particularly applicable is one containing about 0.9% to 3.5% carbon, at least about 1% of at least one alloying element selected from the group consisting of chromium, vanadium, tungsten and molybdenum, and the balance essentially iron, for example, about 40% or 45% or 50% or more iron.

Another composition range is one containing about 0.9% to 3% or 3.5% carbon, about 3% to 15% chromium, up to about 10% or 20% vanadium, up to 25% tungsten, up to about 12% molybdenum, and the balance essentially iron.

A composition particularly advantageous in producing high carbon tool steels of the chromium-vanadium-tungsten variety, including the high speed steel varieties, is one containing about 3% to 9% chromium, 0.3% to 10% vanadium, 1% to 25% tungsten, up to 10% molybdenum, and the balance essentially iron.

The foregoing ranges stated hereinabove may contain optionally up to about 2% silicon, up to about 2% manganese, up to about 5% nickel, and up to about 15% cobalt.

One aspect of the invention resides in a powder metallurgy method of producing a wrought, high carbon tool steel alloy product characterized by a substantially uniform composition throughout and a uniform dispersion of finely divided carbide substantially free from segregates and/or aggregates. The method comprises providing a batch of wrought, composite, mechanically alloyed, dense metal particles, substantially each of said particles being comprised of a plurality of alloyable constituents formulated to a desired high carbon tool steel composition as set forth hereinbefore (note, for example, Tables I and II), at least one of the constituents being a compressible metal, such as iron. The composite particles are characterized metallographically by an internal structure com-

prising said constituents intimately united and interdispersed. The batch of particles is then hot consolidated to a wrought metal shape, whereby the wrought shape is characterized substantially throughout by composition uniformity and a high degree of dispersion uniformity of finely divided carbide in both the longitudinal and transverse directions.

One method of hot consolidating the batch of particles is to vacuum pack composite particles in a mild steel can which is then welded shut, followed by hot extruding the canned powder at an elevated temperature of at least about 1500° F., for example at 1900° F. to 2300° F.

In working with metals which melt above 1000° K., the heavy cold work imparted to the composite metal particle during its preparation is particularly advantageous in the production of uniform compositions by solid state diffusion at elevated temperatures. Observations on other alloy systems have indicated that the heavy cold work increases effective diffusion coefficients in the product powder. This factor, along with the intimate mixture in the product powder of metal fragments from the initial components to provide small interdiffusion distances, promotes rapid homogenization and alloying of the product powder upon heating to homogenizing temperatures. The foregoing factors are of particular value in the production of complex high carbon high alloy tool steels in which diffusion tends to be sluggish. Homogenization and/or annealing can be accomplished, for example, during the heating of canned powders prior to extrusion.

One of the advantages of formulating compositions in accordance with the invention is that very little or no oxidation occurs during high energy milling. However, unlike the kind of oxidation which occurs in conventional melting techniques, any extraneous oxides appear as fine dispersoids and can be useful as dispersion strengtheners, provided they are relatively chemically stable and temperature resistant.

Thus, by producing composite metal powders in accordance with the foregoing, particles of substantially uniform composition are provided from which wrought metal products can be produced by hot consolidating a batch (e.g., a confined batch) of the particles to a desired shape, such as by hot extrusion. Each particle is in effect a building block exhibiting optimum metallographic uniformity, which uniformity is carried forward into the final product unlike previous powder metallurgical methods. In other words, in the case of the carbide-forming constituents, these constituents are fixed uniformly in position in the particle so that upon interdiffusion at an elevated temperature, finely divided carbide particles are formed uniformly dispersed throughout the end product produced from the composite powder.

As illustrative of the use of the invention in producing high carbon tool steel products, the following examples are given:

EXAMPLE I

As indicated hereinbefore, one of the advantages of the method provided by the invention is that high carbon-containing alloys, such as tool steels, may be produced whole avoiding the problem of forming carbide dendrites or segregates which normally attend such alloys when produced by conventional melting and casting techniques. An example of one composition is the rather complex high speed tool steel containing 20% tungsten, 12% cobalt, 4% chromium, 2% vanadium, 0.8% carbon and the balance essentially iron. In producing the composition, a mixture of the constituents is placed in a high energy mill of the type illustrated in FIG. 2 containing a charge of approximately ¼ inch hardened steel balls at a ball-to-power volume ratio of about 20 to 1. The powder is dry milled at an impeller speed of 180 r.p.m. until composite metal particles are formed cold worked to substantially saturated hardness and the milling continued for a time sufficient to obtain an internal struc-

ture within the particles in which the constituents are intimately united and homogeneously interdispersed. The powder is thereafter vacuum sealed in a mild steel can and extruded at a temperature of about 2150° F. at an extrusion ratio of 16 to 1. The steel produced in this way, unlike to conventionally produced steel, will be free of carbide dendrites, segregates and/or aggregates.

An advantageous method in producing the foregoing composition is to make a blend of 28.6 grams of a 70% vanadium 30% iron master alloy powder passing 100 mesh, 57.2 grams of a 70% chromium-30% iron master alloy powder passing 100 mesh, 200 grams of tungsten powder of 10 micron average particle size, 120 grams of cobalt powder passing 325 mesh, 8 grams of graphite passing 100 mesh and 586 grams of sponge iron powder of about 65 micron average size. This mixture is placed in the attritor mill and milled for about 40 to 50 hours at about 180 r.p.m. using a charge of one-quarter inch hardened steel balls, the ball charge being sufficient to provide a volume ratio of balls to powder mixture of about 20 to 1. The 40 to 50 hour milling is generally sufficient to produce composite particles characterized metallographically by a microstructure comprising a substantially homogeneous interdispersion of all of the constituents. The resulting powder is hot extruded as described hereinabove.

The complex high speed steel of Example I is hardened by heating to a temperature of about 2350° F. for about 5 to 10 minutes followed by oil quenching to room temperatures, the cooled steel being thereafter subjected to double tempering by a temperature of about 1050° F. for about 2 hours.

EXAMPLE II

In producing a wrought high carbon steel containing about 0.85% carbon, about 0.2% chromium, about 0.7% manganese, about 0.3% silicon and the balance essentially iron, the following method is employed:

A brittle high carbon master alloy is produced containing about 4.25% carbon, about 1% chromium, about 3.5% manganese, about 1.5% silicon and the balance essentially iron. The master alloy is chill cast and then crushed to pass 200 mesh. The crushed high carbon master alloy in an amount of 400 grams is mixed and uniformly blended with 1600 grams of high purity sponge iron of about 65 microns in size. The mixture is placed in the mill of the type described in Example I containing a charge of one-quarter inch diameter hardened steel balls at a ball-to-powder ratio of about 18 to 1 by volume. The charge is dry milled at an impeller speed of about 175 r.p.m. until a highly cold worked composite metal powder is obtained after about 45 hours of milling characterized by a microstructure comprising a substantially homogeneous interdispersion of all of the alloying constituents. The powder is thereafter annealed and employed in the hot extrusion of wrought tool steel shapes. The composite powder is vacuum packed in a mild steel can which is welded shut. The can is heated to 2000° F. and then hot extruded to a round rod at an extrusion ratio of about 16 to 1. The extruded product is surface cleaned.

As stated hereinbefore, the extruded high carbon tool steel products made in accordance with the invention are characterized metallographically by being free from carbide segregates and/or aggregates as well as exhibiting optimum response to heat treatment. The steel of Example II is hardened by oil quenching from an austenitizing temperature of about 1450° F., followed by tempering at a temperature of about 350° F.

EXAMPLE III

A wrought semihigh speed steel composition can be produced in accordance with the invention having the following composition: about 1.2% carbon, about 4% chromium, about 3% vanadium, about 4% molybdenum, about 0.3% manganese, about 0.3% silicon and the bal-

ance essentially iron. As in Example II, a brittle high carbon master alloy having the following composition is first produced: about 4.8% carbon, about 16% chromium, about 12% vanadium, about 12% molybdenum, about 1.2% manganese, about 1.2% silicon and the balance iron. The master alloy is chill cast and then crushed to pass 200 mesh. About 400 grams of the crushed master alloy are mixed with 1200 grams of high purity sponge iron of about 65 microns in size. The mixture is placed in the mill of the type described in Example I containing a charge of one-quarter inch diameter hardened steel balls at a ball-to-powder ratio of about 18 to 1 by volume. The charge is dry milled at an impeller speed of about 175 r.p.m. until a highly cold worked composite metal powder is obtained after about 48 hours of milling characterized by a microstructure comprising a substantially homogeneous interdispersion of all of the alloying constituents. The powder is thereafter employed in the hot extrusion of wrought tool steel shapes. The composite powder is vacuum packed in a mild steel can which is welded shut. The can is heated to 2000° F. and then hot extruded to a square rod at an extrusion ratio of about 15 to 1. The extruded product is then surface cleaned. A tool made from the product produced hereinabove may be heat treated by quenching from about 2250° F. in oil and then tempered (secondary hardening) by heating to about 1000° F. and holding for about one hour. The steel produced in accordance with the invention will exhibit good response to heat treatment.

EXAMPLE IV

In producing a wrought very high carbon, high speed steel containing about 2.5% carbon, about 4% chromium, about 7% vanadium, about 6% tungsten, about 2.5% molybdenum, about 5% cobalt, and the balance essentially iron, the following method was employed:

A powder blend consisting of 112.5 grams of graphite flakes passing 100 mesh, 432 grams of a 70% vanadium-30% iron master alloy powder passing 100 mesh, 180 grams of chromium powder passing 100 mesh, 113 grams of molybdenum powder passing 325 mesh, 225 grams of cobalt powder passing 325 mesh, 270 grams of tungsten powder of about 10 microns average particle size and 3191 grams of sponge iron powder of 65 microns size is placed in a ball mill having a driven impeller and containing 200 pounds of 3/8 inch diameter hardened steel balls and processed for 15 hours at 246 r.p.m. in a nitrogen atmosphere. At the end of this time a highly cold worked composite metal powder is obtained characterized by a microstructure comprising a substantially homogeneous interdispersion of all the alloying constituents. The composite powder is vacuum packed in a mild steel can which is welded shut. The can is heated to 2000° F. and then hot extruded to a rod at an extrusion ratio of about 16 to 1. The hardness of the extruded bar was found to be 62.5 Rc. The structure of the extruded material was very homogeneous with not more than 10% by volume of the structure being segregated regions exceeding 25 microns in minimum dimension. A tool or die made from the foregoing product is hardened by heating slowly to 1600° F., raising the temperature to 2200° F., holding for 5 minutes and oil quenching. It is then double tempered for 2 hours at 1000° F. followed by air cooling.

The hardness of the material is found to be as high as 67 Rc.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and the appended claims.

I claim:

1. As a powder metallurgy article of manufacture, a wrought, high carbon tool steel shape having a composition containing by weight about 0.7 to 4% carbon, at least about 0.1% of at least one alloying element selected from the group consisting of chromium, vanadium, tungsten and molybdenum, and the balance essentially iron in an amount of at least about 55%, said wrought steel shape being characterized substantially throughout by composition uniformity, optimum heat treating response and by a high degree of dispersion uniformity of finely divided carbides substantially free of carbide segregates and aggregates such that less than 10 volume percent of segregated regions exceeding 25 microns in minimum dimension is present.

2. The article of manufacture of claim 1, wherein the carbon content ranges from about 0.9 to 3.5%.

3. The article of manufacture of claim 2, wherein said composition includes optionally up to about 2% silicon, up to about 2% manganese, up to about 5% nickel and up to about 15% cobalt.

4. The article of manufacture of claim 2, wherein the composition contains about 0.9 to 3.5% carbon, about 3 to 15% chromium, up to about 20% vanadium, up to about 25% tungsten and up to about 12% molybdenum.

5. The article of manufacture of claim 4, wherein the composition contains about 0.9 to 3.5% carbon, about 3 to 9% chromium, about 0.3% to 10% vanadium, about 1 to 25% tungsten, up to about 10% molybdenum, up to about 2% silicon, up to about 5% nickel and up to about 15% cobalt.

6. The article of manufacture of claim 1 substantially free of carbide segregates and aggregates such that less than 10 volume percent of segregated regions exceeding 10 microns in minimum dimension is present.

7. The article of manufacture of claim 2 containing at least 1% of at least one alloying element selected from the group consisting of chromium, vanadium, tungsten and molybdenum.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,591,349

Dated July 6, 1971

Inventor(s) JOHN STANWOOD BENJAMIN

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 1, line 57, for "insobluble" read --insoluble--.

Line 62, for "alloyng" read --alloying--.

Col. 2, line 10, for "partically" read --practically--.

Col. 7, line 69, for "ductible" read --ductile--.

Col. 8, Table II, for "Tungsten-cobalt types", last number under "Co" (last column), for "11.-12.25" read --11.5-12.25--.

Same Table, for "Tungsten-molybdenum types", first number under "C" (first column), for "1.05-1.1" read --1.0-1.1--.

Col. 9, line 3, for "he" read --the--.

Line 61, for "whole" read --while--.

Line 71, for "ball-to-power" read --ball-to-powder--.

Signed and sealed this 31st day of October 1972.

(SEAL)

Attest:

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